

PATENT SPECIFICATION

945,834



NO DRAWINGS

945,834

Date of Application and filing Complete Specification: Dec. 27, 1961.

No. 46179/61.

Application made in United States of America (No. 111,470) on May 22, 1961.

Complete Specification Published: Jan. 8, 1964.

© Crown Copyright 1964.

Index at acceptance:—Classes B2, B(4B, 4C, 4X); C3, B(1C8, 1D2C, 1N1A, 1N1F, 1N16B); C3, R(1C8, 1C16, 2C8, 2C16, 22C11, 22D1A, 22D2B, 22D6, 22PX, 22T2, 29C8, 29C16).

International Classification:—B 05 (C 08 g).

COMPLETE SPECIFICATION

Method for Insulating Conductors

We, SHAWINIGAN RESINS CORPORATION, a Corporation organised and existing under the laws of the Commonwealth of Massachusetts, United States of America, of Springfield, Commonwealth of Massachusetts, United States of America (assignees of

EDWARD LAVIN, ALBERT HENRY MARKHART and CHARLES FRASER HUNT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to enameled wires. In particular the present invention relates to wires coated with a plurality of layers of oleoresinous materials, epoxide resin compositions or acrylic polymers, and polyimide resin compositions.

It is well known that magnet wires may be made by coating copper wire with any one of a wide variety of natural and synthetic organic polymers. These include oleoresinous materials, epoxide resin compositions and acrylic polymers. While the vast assortment of such wires covers a very broad spectrum of properties, the ultimate use to which a given wire will be applied depends on the balance of electrical, chemical and mechanical properties possessed by the particular wire. In this respect, a common defect of the three types mentioned is short dielectric life at elevated temperatures, e.g. 300°C.

On the other hand, a magnet wire coated with certain aromatic polyamides which are converted to polyimides upon curing in a wire-coating oven, has been shown to have a much higher thermal life than that of the above mentioned types. A defect of this wire, however, is that its coating tends to craze when it has not been properly annealed and the crazing, once it has occurred, will not heal with further heat treatment. Polyimide wires present the further disadvantage that the application of the enamel requires a rather

expensive solvent system as compared to that used with more common enamels.

It is therefore an object of this invention to produce a magnet wire with improved dielectric stability at high temperatures. Another object is to achieve this improvement without unduly sacrificing any of the other electrical, chemical and mechanical properties that a magnet wire must possess, such as flexibility, good enamel adherence to metal, and others.

According to the present invention a thin layer of a polyamide enamel which is convertible into a polyimide upon curing is applied over or under several coats of "plain" enamel (as the oleoresinous materials are commonly known), epoxide resin compositions or acrylic polymers. In so doing, it has been observed that the thermal life of the combination coating is considerably longer, at high temperatures, than that of any of the mentioned enamels alone. In fact, an unexpected synergism is found to operate which boosts the thermal life of the combination wires beyond what could be expected from simple addition of the protection provided by each enamel individually.

According to the present invention there is provided a metal conductor coated with a plurality of layers of a polyimide composition comprising the polymeric condensation product of an aromatic tetracarboxylic acid with an aromatic diamine containing from 6 to 16 carbon atoms or a saturated aliphatic diamine containing up to 6 carbon atoms, and another cured organic composition which is (1) a plain oleoresinous wire enamel, (2) an epoxy enamel comprising a high molecular weight epoxide resin, a fusible condensate of an aldehyde with an organic ammonia derivative selected from an amine or amide having reactive hydrogen, and a polyhydric phenol, or (3) an acrylic enamel applied as an aqueous dispersion of an interpolymer obtained by the polymerization of

50

55

60

65

70

75

80

85

90

acrylonitrile with an α -olefinic monocarboxylic acid and an ester of said acid with a 1 to 8 carbon atom saturated aliphatic monohydric alcohol, blended with a dispersion of a heat reactive condensation product of an aldehyde with a phenol or an organic derivative of ammonia such as urea and melamine. These condensate resins but for their possible content of a phenol are identical to those mentioned above for admixture with the epoxide enamels. They are hereinafter referred to as heat reactive aldehyde condensate resins. 5

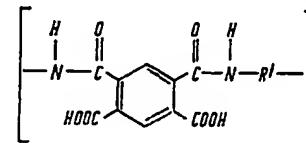
Any of the "plain enamels" available commercially may be used. The term "plain oleoresinous enamel" has acquired respectable currency in the trade. It encompasses a very large class of wire enameling preparations which have been, by and large, rather poorly described in the technical literature. They are best identified by two common characteristics: (1) they belong mostly to the same standard thermal stability class, namely class 105°C., as defined in the 1957 Revised Standard No. 1 of the American Institute for Electrical Engineers (see Staff Report, ELECTRICAL MANUFACTURING, August, 1957, page 112); (2) they are prepared by chemically combining under heat natural resins and drying oils. The natural resins employed include copal, shellac and resin. Among the drying oils that may be used are tung oil, raw or alkali refined linseed oil, perilla oil, safflower oil and oiticica oil. Some of the commercial plain enamels also contain, in addition to or in lieu of the natural gums and resins, synthetic resins such as phenol-formaldehydes, melamine-formaldehydes and alkyd resins made of a phthalic acid glyceride which may or may not contain a drying oil. 10

The usable epoxy enamels are those falling within AIEE thermal class 130°C. They can be characterised as complex compositions of high molecular weight epoxide resins and fusible condensates formed by the partial reaction of aldehydes, particularly formaldehyde, with organic ammonia derivatives which may be amines or amides and which include urea, thiourea, substituted ureas, melamine, aminotriazines and aminodiazines. The complex epoxide resins are polyether derivatives of a polyhydric phenol containing epoxide groups and are free from functional groups other than epoxide and hydroxyl groups. The compositions also contain polyhydric phenols and, usually, other ingredients such as resins, e.g. polyvinyl formal and catalysts. The proportions of the components may vary substantially but must remain such that the initial reaction products are capable of further reaction on the coated substrate to form insoluble and infusible products. Satisfactory proportions are afforded by the range of from equal amounts by weight of complex epoxide 15

and aldehyde ammonia derivative condensate resin to 9 parts by weight of complex epoxide to 1 part by weight of aldehyde condensate. 20

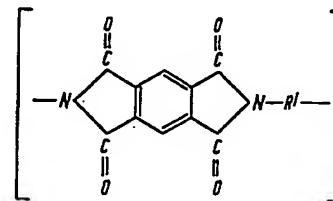
The acrylic enamels which may be employed in the practice of this invention consist of an aqueous dispersion of an acrylic interpolymer blended with a solution or dispersion of a heat reactive aldehyde condensation resin such as a phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde or urea-melamine formaldehyde resin. The interpolymer is obtained by the polymerisation of acrylonitrile, an α -olefinic monocarboxylic acid and an ester of said acid with a 1-8 carbon atom saturated aliphatic monohydric alcohol and if desired, a glycidyl ester of said acid with 2, 3-epoxy-propanol-1 or allyl glycidyl ether. The most satisfactory acrylic enamels are dispersions of an interpolymer of monomers consisting of 30 to 80 parts by weight of acrylonitrile, 2 to 15 parts by weight of acrylic acid, methacrylic acid, ethacrylic acid, phenylacrylic acid or crotomic acid and 18 to 35 parts by weight of an ester of said α -olefinic monocarboxylic acids with a saturated aliphatic monohydric alcohol having 1 to 8 carbon atoms for a total of 100 parts by weight and a water dilutable heat reactive phenol-formaldehyde resin, urea-formaldehyde resin, urea-melamine-formaldehyde resin, or melamine-formaldehyde resin, said composition being insoluble in a boiling mixture of equal volumes of toluene and ethyl alcohol. 25

The polyamides useful in this invention are the condensation products of tetracarboxylic aromatic acids with diamines and may be illustrated by the recurring structural unit 30



105

These polymers are soluble, and can be converted *in situ* by further heating into polyimide structures that are extremely resistant to solvents:



110

The pyromellitic acid residue incorporated in these formulae can be replaced of course with two ring tetracarboxylic acids, provided that the carboxylic groups of the latter compounds are arranged in two o-phthalic configurations. 115

Meeting these requirements are, for example, the tetracarboxylic acids corresponding to naphthalene, diphenyl methane, 2,2'-diphenyl propane, diphenyl ether, diphenyl sulfide and diphenyl sulfone. The R¹ of the formulae stands for a divalent radical of either benzene, naphthalene, biphenyl, diphenyl ether, ditolyl ether, diphenyl sulfide, diphenyl sulfone, diphenyl methane, 2,2'-diphenyl propane, benzophenone, or from a low molecular weight saturated aliphatic hydrocarbon containing not more than six carbon atoms. 5

The preferred polyamides are the condensation products of pyromellitic dianhydride with a diamine characterized by a lack of aliphatic hydrogen atoms and by the possession of a flexible linkage such as the ether group of 4,4'-oxydianiline. These polyamides should preferably be such that they show a viscosity ranging from about 1300 centipoises to 5000 centipoises for a 15% by weight solution in 1:1 dimethylacetamide and N-methylpyrrolidone at 25°C. 10

The actual composition of the enamels employed, the number of layers of each enamel applied, the order of application of different enamels and the cure temperature are factors which must necessarily vary according to the balance of properties that the contemplated wire is to ultimately possess. Nevertheless, if the above described compositions are used in the recommended combinations, the improvement in thermal life which is the essence of this invention 15 will be achieved despite the net effect of the interplay of such factors, provided that the latter are not allowed to vary beyond the following limits:

As to the enamel cure temperature, it can range from 250° to 500°C. depending, among other things, on the type of enamels used and the speed of the wire through the curing tower. 20

The preferred number of coats of enamels are two and four for the polyamide and the other organic enamel respectively. This is for a "heavy build" magnet wire. Depending upon the diameter of the wire to be coated, the viscosity of the enamel solutions to be employed and the conditions under which the finished wire will be used, insulation of any thickness between 0.1 to 4.0 mils may be applied in 2 to 14 layers. In view of this, it is evident that no restriction 25 to the two and four distribution of different enamel coats that is favoured for heavy build wire is intended.

Various other materials such as fillers, plasticizers and coloring agents as well as minor amounts of other resins, may be incorporated into these enamels as is often done conventionally. 30

These new combinations of enamels may be used on any size of wire, on a variety of metals and on other materials. Non- 35

electrical uses are also indicated where temperature stability, smoothness and flexibility are, among other properties, required of a synthetic finish. 40

The present invention will be further illustrated by way of the following examples in which five different enamels were used: one oleoresinous, one epoxy, one acrylic, and two polyamide compositions. All but one of these enamels are commercially available. 45

Oleoresinous or "plain" enamel has been a standard insulation for some 50 years. It is prepared by chemically combining under heat natural resins and drying oils, usually tung oil. The particular preparation used here is available under the commercial designation "Hi T.S. Enamel No. 585". 50

The epoxy enamel used is sold as "Epi Rez 2184". It is based on a high molecular weight epoxide resin derived from bisphenol A and epichlorohydrin. The composition most probably also contains from 15 to 30% of a urea-formaldehyde resin, a certain quantity of polyvinyl formal and a Lewis type acid catalyst system. 55

The acrylic enamel is a water dispersion of an interpolymer of monomers consisting of acrylonitrile, an α -olefinic monocarboxylic acid, an ester of such acid with an aliphatic saturated monohydric alcohol, and a water-dilutable, heat-reactive aldehyde condensation resin. The particular enamel used here is marketed under the designation "Lecton" (a Registered Trade Mark). 60

One of the polyamides employed in the examples (polyamide A), is the condensation product of pyromellitic dianhydride with 4,4'-oxydianiline. The oxydianiline was recrystallized from ethyl alcohol - dimethyl acetamide, and technical pyromellitic dianhydride was purified by heating at 250°C. for two hours at 80 mm pressure. The resulting pyromellitic dianhydride, 14.8 g, was slurried in 71 ml dry dimethyl acetamide in a three-neck, round-bottom flask fitted with a thermometer and an air condenser, protected with a calcium chloride tube. A solution of 13.4 g oxydianiline in 71 ml dry N-methylpyrrolidone was added. The reaction mixture was held at 50°C. for two hours. The polyamide solution thus obtained was applied on wire. Suffice it to say at this stage that the polyamide, after it has been applied to the wire, is converted *in situ* to a polyimide structure during the subsequent processing of the wire. 65

The other polyamide enamel used in the examples, polyamide B, is a commercial product marketed under the brand name "ML": it consists essentially of a polyamide chemically similar to that in polyamide A, dissolved as a 15% by weight solution in a mixture of N-methylpyrrolidone and dimethyl acetamide and having a viscosity of about 4800 centipoises at 25°C. 70

75

80

85

90

95

100

105

110

115

120

125

130

EXAMPLES 1—4.

5 The enamels were applied to number 18 (0.0403 inch) copper wire by conventional wire coating means, each layer of enamel being cured by passing the dipped wire through a vertical oven 12 feet high with a set cure temperature of 390°C. at a constant rate of speed selected from the range of 13 to 19 feet of wire per minute. A split applicator was employed so that the desired number of different coats could be put on in one continuous operation.

10 Control wires were prepared with the oleoresinous, the epoxy and the acrylic enamels by applying six successive coats of the enamels to the bare wire. Since each coat has a thickness of approximately 0.25 mils, the resulting wires were thus given a "heavy build", i.e. they had a diameter approximately 3.0 mils larger than that of the bare original wires. In the case of the polyamides, only one two-coat control wire with a build of approximately 1 mil was deemed sufficient.

15 20 The testing of the enameled wires was

done by standard procedures. Although numerous chemical, physical and electrical properties of the control wires and of the new insulated wires were tested, the description of the testing procedures will be limited to that measuring the property in which significant changes were observed, namely the one-kilovolt life test.

25 30 *1 Kilovolt-life Test.* The 1 Kv-life test was made in accordance with the provisions of the American Institute of Electrical Engineers specification No. 57, dated October, 1955. The test is a measure of the period for which a coating can be exposed at the particular temperature indicated before it will fail as electrical insulation upon the application of 1000 volts for one second to the sample. Ten samples are used in each test.

35 40 45 Table I shows the significant properties of the control wires coated with standard enamels. The figures will serve as a basis for evaluating the new insulations of the latter examples.

TABLE I — CONTROL ENAMELS

Example	Enamel	Build (mils)	1 KV Life (hours)	
			250°C.	300°C.
1	Oleoresinous	3	28	3
2	Epoxy	3	73	10
3	Acrylic	3	25	2
4	Polyamide B	1	50	27

EXAMPLES 5—12.

50 55 Wires were then prepared with insulation consisting of two contiguous coats of a polyamide composition placed under or over four

contiguous coats of any one of the oleoresinous, epoxy or acrylic enamels. The relevant properties of these new wires are summarized in Table II.

TABLE II — COMBINATION ENAMELS

Example	Enamel	Build	1—KV Life (Hours)	
			(mils)	
5	Oleoresinous over Polyamide B	2 + 1	365	35
6	Epoxy over Polyamide B	2 + 1	612	140
7	Acrylic over Polyamide B	2 + 1	560	65
8	Oleoresinous over Polyamide A	2 + 1	320	32
9	Polyamide B over Oleoresinous	1 + 2	250 ¹⁰	60 ¹⁰
10	Polyamide B over Epoxy	1 + 2	250 ¹⁰	60 ¹⁰
11	Polyamide B over Acrylic	1 + 2	250 ¹⁰	42
12	Polyamide A over Acrylic	1 + 2	250 ¹⁰	49

(NOTE: the values accompanied by a superscript are not final in that at the time indicated by the figure, e.g. 250 hours in example 9 at 250°C., a number of samples represented by the superscript, 10 in this case, were still resisting the conditions of the test. Since the final values, in such cases, will necessarily be larger than those reported here, the invention is clearly described by the latter values.)

5 A comparison of these results with those for the control wires shown in Table I unquestionably demonstrates that the thermal life of any of the combination coatings is longer than not only that of each enamel entering in the combination but is also longer than the hypothetical value which might have been predicted by adding the protection afforded by each individual enamel. For instance, looking at the acrylic-polyamide B system, where the component enamels have 250°C. lives of 25 and 50 hours respectively (Table I, Examples 3 and 4) it would have 35

10 been expected that the combination wire would have a life of 75 hours at that temperature; instead, as shown by examples 7 and 11, the lives of the combination wires proved to be 560 hours in the case of the acrylic overcoat and more than 250 hours in the case of the polyamide overcoat. A synergistic effect therefore accounts for those surprising results. 40

15 **WHAT WE CLAIM IS:—** 45

20 1. A metal conductor coated with a plurality of layers of a polyimide composition comprising the polymeric condensation product of an aromatic tetracarboxylic acid with an aromatic diamine containing from 6 to 25

25 16 carbon atoms or a saturated aliphatic diamine containing up to 6 carbon atoms, and another cured organic composition which is (1) a plain oleoresinous wire enamel, (2) 50

30 an epoxy enamel comprising a high molecular weight epoxide resin, a fusible condensate of an aldehyde with an organic ammonia derivative selected from an amine or amide having a reactive hydrogen, and a polyhydric phenol, or (3) an acrylic enamel applied as an aqueous dispersion of an interpolymer obtained by the polymerization of acrylonitrile with an α -olefinic monocarboxylic acid and an ester of said acid with a 1 to 8 carbon atom saturated aliphatic monohydric alcohol, blended with a dispersion of a heat reactive aldehyde condensate resin as hereinbefore defined. 55

35 2. A conductor as claimed in claim 1 in which the plain oleoresinous wire enamel is the reaction product obtained by heating copal, resin or shellac, with tung oil, raw linseed oil, alkali refined linseed oil, perilla oil, safflower oil or oiticica oil. 60

40 3. A conductor as claimed in claim 1 in which the fusible condensate of an aldehyde with an organic ammonia derivative of the epoxide enamel is a formaldehyde amine or a formaldehyde amine resin. 65

45 4. A conductor as claimed in claim 1 or 3 in which the epoxy enamel is a complex reaction product obtained by heating a fusible resinous condensate of an aldehyde with an amine or amide, with a complex epoxide which is a polyether derivative of a polyhydric phenol containing epoxide groups and

free from functional groups other than epoxide and hydroxyl groups, the proportions being within the range of from equal amounts by weight of complex epoxide and aldehyde condensate to 9 parts of complex epoxide and 1 part of aldehyde condensate. 5. A conductor as claimed in any of claims 1, 3 or 4 in which the condensate of an aldehyde with an organic ammonia derivative of the epoxide enamel is a urea-formaldehyde or melamine formaldehyde resin. 6. A conductor as claimed in claim 1 in which the aldehyde condensate resin of the acrylic enamel is a phenol formaldehyde, an urea formaldehyde, a melamine formaldehyde resin, or a urea melamine formaldehyde resin. 7. A conductor as claimed in claim 1 or 6 in which the acrylic enamel is an aqueous dispersion of an interpolymer of monomers consisting of 30 to 80 parts by weight of acrylonitrile, 2 to 15 parts by weight of acrylic acid, methacrylic acid, ethacrylic acid, phenyl acrylic acid or crotonic acid, and 18 to 35 parts by weight of an ester of said α -olefinic monocarboxylic acids with a saturated aliphatic monohydric alcohol having from one to 8 carbon atoms for a total of 100 parts by weight and a water-dilutable heat-reactive phenol-formaldehyde resin, urea-formaldehyde resin, urea-melamine-formaldehyde resin and melamine-formaldehyde resin, said composition being insoluble in a boiling mixture of equal volumes of toluene and ethyl alcohol. 8. A conductor as claimed in any of the preceding claims in which the aromatic tetracarboxylic acid of the polyamide is pyromellitic acid. 9. A conductor as claimed in any of the preceding claims in which the polyimide is the polymeric condensation product of pyromellitic anhydride with 4,4'-oxydianiline. 10. A conductor as claimed in any of the preceding claims coated with insulation of a thickness of 0.1 to 4.0 mils consisting of 2 to 14 layers of the resins. 11. A conductor as claimed in any of the preceding claims with two coats of the polyimide composition and four coats of the acrylic enamel, epoxy enamel, or plain oleoresinous enamel. 12. A coated metal conductor as claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in any of the Examples. 13. A process for the production of a coated metal conductor as claimed in any of the preceding claims which comprises passing the conductor separately through each of the liquid polyamide and either the liquid plain oleoresinous, epoxy or acrylic enamel compositions and drying and curing each coating at a temperature from 250°C. to 500°C. after passage through each composition. 14. A process as claimed in claim 13 for the production of a coated metal conductor as claimed in any of claims 1 to 12 substantially as hereinbefore described with reference to and as illustrated in any of the Examples.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.